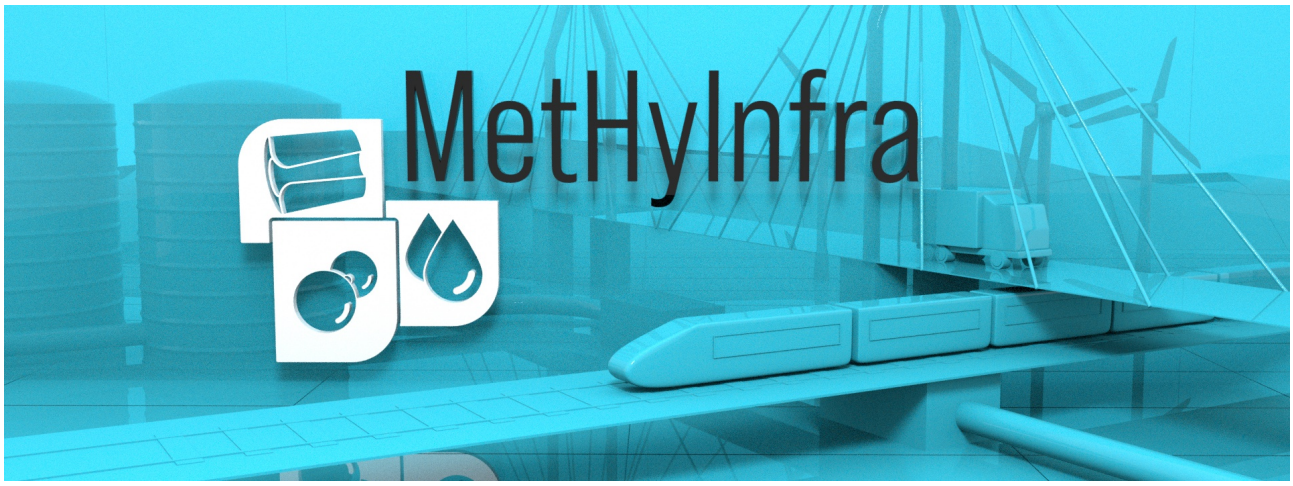

REPORT:
Suitable modeling approaches for the most important influences of real gas effects in high-pressure hydrogen flows

A3.1.2: Report of literature review

Authors: S. Weiss, S. Schmelter

Confidentiality: Public

Submission date: 25.05.2022

Revision: 1.0

methyinfra.ptb.de

Report on suitable modeling approaches for the most important influences of real gas effects in high-pressure hydrogen flows (A3.1.2)

Funding	**Grant agreement no:**
European Metrology Program for Innovation and Research	20IND11
Project name	**Project short name**
Metrology infrastructure for high-pressure gas and liquified hydrogen flows	MetHyInfra

Author(s)			**Pages**
S. Weiss	PTB	sebastian.weiss@ptb.de	8 pages
S. Schmelter	PTB	sonja.schmelter@ptb.de	

Summary

This report on suitable modeling approaches for the most important influences of real gas effects in high-pressure hydrogen flows was written as part of activity 3.1.2 from the EMPIR Metrology infrastructure for high-pressure gas and liquified hydrogen flows (MetHyInfra) project. The three-year European project commenced on 1st June 2021 and focused on providing metrological infrastructure and traceability for high pressure hydrogen flow meter calibration (1000 bar / 3.6 kg/min), fuel cells applications (4 kg/h, 30 bar) and liquid hydrogen. For more details about this project please visit methyinfra.ptb.de.

This report reviews different modeling approaches to account for the most relevant real gas effects in high-pressure hydrogen flows with the special focus on critical nozzle flow. It summarizes the important physical properties that are affected by real gas effects, presents several real gas modeling approaches, and compares them with ideal gas models. Furthermore, this report highlights the importance of a time-efficient as well as accurate implementation of real gas models when used in CFD software.

Confidentiality	Public

This project (20IND11 MetHyInfra) has received funding from the EMPIR programme co-financed by the Participating States and from the European Union's Horizon 2020 research and innovation programme.

The EMPIR initiative is co-funded by the European Union's Horizon 2020 research and innovation programme and the EMPIR Participating States

Contents

1 Introduction

This report summarizes the Activity A3.1.2 of the EMPIR 20IND11 MetHyInfra project. A literature study was performed on suitable modeling approaches for the most important influences of real gas effects in high-pressure hydrogen flows (up to 100 MPa) with the special focus on critical nozzle flow. Different modeling approaches are reviewed and compared in this report.

To determine the relevant real gas effects in high-pressure hydrogen flows, it is important to understand the difference between ideal and real gases. In an ideal gas, particles have no volume, collisions between particles are elastic, and there are no intermolecular forces between them. In contrast, in a real gas, particles have a volume, collisions are non-elastic, and intermolecular forces are existing.

Under standard conditions for pressure and temperature, hydrogen behaves like an ideal gas, i. e., it follows the rules of the ideal gas law. However, in specific ranges for pressure and temperature, the real gas hydrogen deviates from the ideal gas behavior leading to erroneous predictions of its thermodynamic and transport properties.

At high pressure, the distance between gas particles becomes smaller and particle interactions as well as the particle volume are relevant and cannot be neglected as in the case of an ideal gas. At low temperatures, gas particles have less kinetic energy so that energy losses during particle collisions are important to consider. Consequently, real gas effects especially appear at high pressures and low temperatures. For that reason, the ideal gas law is not sufficient to describe high-pressure hydrogen flows precisely.

In hydrogen flows through critical nozzles at high pressures, real gas effects, like van der Waals forces, compressibility effects, variable specific heat capacities, and the Joule-Thomson effect, can occur and therefore need to be captured by a real gas model. Thus, this review of suitable modeling approaches focuses on the consideration of those real gas effects and their influence on the flow behavior in critical nozzles operated with hydrogen.

2 Equation of State (EoS)

An equation of state (EoS) is a thermodynamic equation that relates the physical properties of a fluid, like pressure p, temperature T, and density ρ, with each other and can generally be written as:

$$f(p, T, \rho) = 0. \tag{1}$$

In the following, different EoS models are presented and compared.

2.1 Ideal gas EoS

The ideal gas EoS is given as follows:

$$p \cdot V_m = R \cdot T \quad \text{with} \quad V_m = \frac{M}{\rho}, \tag{2}$$

where p, T, V_m, ρ, M, and R are pressure, temperature, molar volume, density, molar mass, and the universal gas constant, respectively. It is a good approximation for gases at low pressures and moderate temperatures. In order to fully describe the behavior of hydrogen at high pressure, the ideal gas EoS is not sufficient. Thus, in the following, different real gas EoS models are shown that can be used for simulating hydrogen flows within this project.

2.2 Cubic EoS

An extension of the ideal gas EoS is represented by cubic EoS models owing their name to the fact that they can be formulated in a cubic function of the molar volume. All cubic EoS approaches are based on the van der Waals EoS and include parameters to allow for intermolecular forces and the effect of particle volume.

One representative is the Peng-Robinson EoS [6] that is given by the formulation:

$$\left(p + \frac{\gamma \cdot A}{V_m^2 + 2B \cdot V_m - B^2}\right) \cdot (V_m - B) = R \cdot T, \tag{3}$$

where the parameters A, B, and γ are substance-specific and can be expressed in terms of the critical properties and the acentric factor. Comparing this equation to the one of the ideal gas in Eq. (2) shows additional terms expressed in pressure and molar volume considering the intermolecular forces as well as the particle volume, respectively. The Peng-Robinson EoS is the only preinstalled real gas EoS in the OpenFOAM software.

2.3 Empirical fundamental EoS

Empirical fundamental EoS models are very accurate expressions of the EoS for pure fluids in terms of empirical correlations based on experimental data. They are often formulated in the reduced form of the Helmholtz free energy α:

$$\alpha(\delta,\tau) = \frac{a(\rho,T)}{R\cdot T} \quad \text{with} \quad a(\rho,T) = u - T\cdot s, \quad \delta = \frac{\rho}{\rho_c}, \quad \text{and} \quad \tau = \frac{T_c}{T}. \tag{4}$$

Here, a, u, and s depict the Helmholtz free energy, internal energy, and entropy, respectively. The reduced density δ and inverse reduced temperature τ are scaled with the critical density ρ_c and critical temperature T_c of the considered gas, respectively.

The reduced Helmholtz free energy is typically separated into an ideal α^0 and a residual part α^r:

$$\alpha(\delta,\tau) = \alpha^0(\delta,\tau) + \alpha^r(\delta,\tau). \tag{5}$$

Leachman et al. [4] developed an empirical fundamental EoS based on the Helmholtz free energy for parahydrogen, normal hydrogen, and orthohydrogen for pressures up to 2000 MPa and temperatures up to 1000 K. The expressions for the ideal and residual parts of the reduced Helmholtz energy are as follows:

$$\alpha^0(\delta,\tau) = \ln(\delta) + 1.5\ln(\tau) + a_1 + a_2\tau + \sum_{k=3}^{N} a_k \ln\left(1 - e^{b_k\tau}\right), \tag{6}$$

$$\alpha^r(\delta,\tau) = \sum_{i=1}^{l} N_i\delta^{d_i}\tau^{t_i} + \sum_{i=l+1}^{m} N_i\delta^{d_i}\tau^{t_i}e^{\left(-\delta_i^{p_i}\right)} + \sum_{i=m+1}^{n} N_i\delta^{d_i}\tau^{t_i}e^{\left[\varphi_i(\delta-D_i)^2+\beta_i(\tau-\gamma_i)^2\right]}. \tag{7}$$

The parameters a_k and b_k for the ideal part as well as N_i, d_i, t_i, p_i, φ_i, β_i, D_i, and γ_i for the residual part are optimized according to a nonlinear regression of calculated ideal gas heat capacity data from literature as well as experimental thermodynamic and caloric data for hydrogen, respectively.

The ideal contribution to the reduced Helmholtz free energy in Eq. (6) is physically motivated based on an ideal gas heat capacity equation. The residual contribution in Eq. (7) is composed of three summations, where the first summation is a simple polynomial containing seven terms. The two terms in the second summation contain an exponential density component to improve the prediction in liquid and critical-region properties. The third summation contains five modified Gaussian bell-shaped terms to model the critical region more precisely.

Once the reduced Helmholtz free energy is calculated, other thermodynamic properties, i. e. internal energy, enthalpy, entropy, heat capacity, speed of sound, etc., can be calculated directly, as derived by Span et al. [8] for nitrogen. The required derivatives for hydrogen can be found in the work by Ding et al. [2].

As an example, the equation for the pressure is given below:

$$p\cdot V_m = R\cdot T\cdot\left[1 + \delta\left(\frac{\partial\alpha^r}{\partial\delta}\right)_\tau\right], \tag{8}$$

where $\left(\partial\alpha^r/\partial\delta\right)_\tau$ is the first partial derivative of the residual part of the reduced Helmholtz free energy with respect to the reduced density.

For the simulation of high-pressure hydrogen flows through critical flow Venturi nozzles, an empirical fundamental EoS will be integrated into the OpenFOAM structure within the MetHyInfra project. The EoS for hydrogen by Leachman et al. [4] is already available and provides high-accuracy predictions for the temperature and pressure range required in this project. However, the developed equations contain exponential terms as well as exponents using real numbers that are more time-consuming to calculate in a computer program like OpenFOAM compared to simple arithmetic operations. Since the EoS needs to be calculated on every mesh node in every time step in a CFD simulation, this might slow down the calculation of the flow problem drastically. Therefore, in this project, a new EoS will be developed for hydrogen in a simpler form similar to the EoS by Wagner and Span [10] for methane, argon, and nitrogen. Despite its simplicity the accuracy of the new EoS will be improved regarding the considered temperature and pressure range for the nozzle flow.

3 Transport properties

The three main transport properties in fluid dynamics are dynamic viscosity, thermal conductivity, and mass diffusivity corresponding to the transfer of momentum, energy, and mass, respectively. They appear as proportionality factors in the Newton's law of viscosity, the Fourier's law of heat conduction, and the Fick's law of molecular diffusion, respectively. Since no gas mixture but only pure hydrogen is considered in this project, the mass diffusivity is not relevant and will therefore not be considered in this section.

3.1 Dynamic viscosity

The dynamic viscosity of a fluid describes the resistance to deformation at a given shear force. Based on the kinetic theory of gases, the dynamic viscosity is only a function of temperature for dilute gases. For ideal gases, Sutherland's law [9] can be used to predict the dynamic viscosity μ_s as follows:

$$\mu_s = \frac{A_s \cdot T^{\frac{3}{2}}}{T + T_s}, \tag{9}$$

where A_s and T_s are substance-specific constants. However, at high pressures and consequently high densities, the dynamic viscosity is also dependent on pressure or density, respectively. Muzny et al. [5] developed a experimentally-based correlation for the dynamic viscosity of hydrogen for temperatures up to 1000 K and pressures up to 200 MPa using the following approach

$$\mu(\rho, T) = \mu_0(T) + \Delta\mu_{\text{excess}}(\rho, T) + \Delta\mu_{\text{c}}(\rho, T), \tag{10}$$

where $\mu_0(T)$ is the viscosity contribution for the limit of zero density, which is comparable with μ_s. The excess term $\Delta\mu_{\text{excess}}(\rho, T)$ accounts for the increase in viscosity above the zero density value at elevated density. The last term $\Delta\mu_{\text{c}}(\rho, T)$ considers the behavior of viscosity near the critical point. As this contribution only affects a small temperature and density range near the critical point, the authors omitted this term and did not consider the small region near the critical point. Since the critical nozzle flow in this project will not reach close to the critical point, this approach is suitable for the flow simulation.

3.2 Thermal conductivity

The thermal conductivity is a measure of a material's ability to conduct heat. Similar to the dynamic viscosity, the thermal conductivity only depends on temperature for small densities. In OpenFOAM, an expression for the thermal conductivity k_s of an ideal gas is based on the dynamic viscosity by Sutherland using a modified Eucken equation

$$k_s = \mu_s \left(1.32 \cdot c_v + 1.77 \cdot R_M\right) \quad \text{with} \quad R_M = \frac{R}{M}, \tag{11}$$

where c_v and R_M are the specific heat capacity at constant volume and the specific gas constant, respectively. By analogy to the dynamic viscosity, the density dependence becomes relevant for high pressures and densities. Assael et al. [1] developed a correlation of the thermal conductivity of hydrogen fitted to experimental data in the temperature and pressure range of up to 1000 K and 100 MPa, respectively. The thermal conductivity is expressed as the sum of three independent contributions as

$$k(\rho, T) = k_0(T) + \Delta k_{\text{excess}}(\rho, T) + \Delta k_{\text{c}}(\rho, T). \tag{12}$$

These terms are modeled in the same way as the ones in Eq. (10) for the dynamic viscosity with the exception that the last term is also considered for the thermal conductivity.

4 Flow properties

The real gas behavior also has an influence on relevant flow properties and their calculation. Therefore, two important flow parameters, namely the critical flow factor and the speed of sound, will be discussed hereafter.

4.1 Critical flow factor

The mass flow rate in a critical nozzle can be calculated as

$$\dot{m} = C_D \cdot C^* \cdot A^* \cdot \frac{p_0}{\sqrt{R_M \cdot T_0}}, \tag{13}$$

where p_0 and T_0 are the stagnation pressure and stagnation temperature, respectively. The quantities C_D, A^*, and C^* are the discharge coefficient, the critical area, and the critical flow factor, respectively. The critical flow factor C^* considers the real gas effects of a one-dimensional isentropic nozzle flow from the inlet to the nozzle throat and can be determined as follows

$$C^* = \rho^* \cdot u^* \cdot \frac{\sqrt{R_M \cdot T_0}}{p_0}, \tag{14}$$

where ρ^* and u^* are the density and velocity in the nozzle throat or in the critical area. Using the isentropic relation and the EoS for an ideal gas, Eq. (14) simplifies to

$$C^*_{\text{ideal}} = \sqrt{\kappa \left(\frac{2}{\kappa + 1}\right)^{\frac{\kappa+1}{\kappa-1}}} \quad \text{with} \quad \kappa = \frac{c_p}{c_v}. \tag{15}$$

Suitable modeling approaches for the influences of real gas effects in high-pressure hydrogen flows

Here, κ is the isentropic exponent and c_p and c_v are the specific heat capacities at constant pressure and volume, respectively. For a perfect gas, which is an ideal gas with constant specific heat capacities, the isentropic exponent κ is approximately 1.4 for hydrogen and thus the critical flow factor C^* becomes circa 0.68473.

However, in case of a real gas, the isentropic relation and the EoS for an ideal gas are not valid and therefore, the critical flow factor cannot be expressed in this explicit form. The real critical flow factor needs to be determined iteratively for the isentropic and thus adiabatic flow process between the inlet and the throat of the nozzle. Therefore, the specific entropy and the specific total enthalpy between those two points need to be constant yielding a set of two equations:

$$\left.\begin{aligned} s(p_0, T_0) &= s(p^*, T^*) \\ h(p_0, T_0) &= h(p^*, T^*) + \frac{1}{2}u^{*2} \end{aligned}\right\} \quad p^*, T^* \rightarrow \rho^*, u^* \rightarrow C^*_{\text{real}} \tag{16}$$

The inlet stagnation quantities (index 0) are given whereas the critical quantities (index *) are unknown. The specific entropy and enthalpy can be calculated based on the real gas model in use. The critical velocity is equal to the local speed of sound in a one-dimensional critical nozzle that can also be determined with the real gas model. Hence, this is a system of two equations with two unknowns p^* and T^*, from which the real critical flow function can be determined. In the works of Schley et al. [7] and Ding et al. [2] two iteration procedures for the calculation of C^*_{real} are demonstrated.

4.2 Speed of sound

The speed of sound c, which is relevant for the calculation of the Mach number or of the critical flow factor as discussed in the preceding paragraph, is given as follows:

$$c = \sqrt{\kappa \cdot \frac{p}{\rho}}. \tag{17}$$

For an ideal gas, the isentropic exponent represents the ratio of specific heat capacities:

$$\kappa_{\text{ideal}} = \frac{c_p}{c_v} \quad \rightarrow \quad c = \sqrt{\frac{c_p}{c_v} \cdot \frac{p}{\rho}}. \tag{18}$$

In OpenFOAM, the Mach number is calculated according to the speed of sound using the ideal isentropic exponent. In order to calculate the Mach number for real gases, the isentropic exponent needs to be changed to

$$\kappa_{\text{real}} = \frac{c_p}{c_v} \cdot \left(\frac{\partial p}{\partial \rho}\right)_T \cdot \frac{\rho}{p} \quad \rightarrow \quad c = \sqrt{\frac{c_p}{c_v} \cdot \left(\frac{\partial p}{\partial \rho}\right)_T}. \tag{19}$$

The corresponding formulas can be derived from the work on isentropic exponents for real gases by Kouremenos and Antonopoulos [3].

5 Conclusion

Real gas effects can be understood as the deviating behavior of an actual gas (in this project hydrogen) compared to an ideal gas, which becomes significant for high pressures and low temperatures. In order to predict the physical properties of the actual gas properly in those pressure and temperature ranges, the deviations from an ideal gas need to be included in a real gas model. The physical properties that are affected are thermodynamic, caloric, and transport properties, as well as derived flow quantities. Therefore, all these properties need to be part of a real gas model including an EoS providing the relations for the thermodynamic and caloric properties and models for the relevant transport properties.

For the most modern real gas models, the considered quantity is separated into an ideal and a residual contribution. The residual part accounts for the difference compared to an ideal gas and becomes relevant for high pressures and low temperatures. In most cases, the residual part is fitted to experimental data using empirical formulations without having a physically motivated structure. Those formulations often have a complex structure in order to describe the experimental data with high accuracy for a broad range of temperatures and pressures. As an example, the EoS by Leachman et al. [4] for hydrogen contains exponential terms and real-valued exponents for the temperature and density terms.

For the implementation in a CFD software like OpenFOAM, those complex terms can lead to high simulation times, which can make the CFD calculations infeasible for practical applications. Therefore, in this project, a new EoS will be developed, which uses simple polynomial ansatz functions for density and temperature. Nevertheless, due to enhanced measurement data provided within the project, this approach will be even more accurate in the range that is relevant for nozzle flow compared to other EoS models for hydrogen. Hence, a time-efficient and accurate implementation of a real gas model for hydrogen in OpenFOAM can be realized.

References

[1] M. J. Assael, J.-A. M. Assael, M. L. Huber, R. A. Perkins, and Y. Takata. Correlation of the thermal conductivity of normal and parahydrogen from the triple point to 1000 k and up to 100 MPa. *Journal of Physical and Chemical Reference Data*, 40(3):033101, September 2011. doi: 10.1063/1.3606499.

[2] Hongbing Ding, Chao Wang, and Yakun Zhao. Flow characteristics of hydrogen gas through a critical nozzle. *International Journal of Hydrogen Energy*, 39:3947–3955, 03 2014.

[3] D. A. Kouremenos and K. A. Antonopoulos. Isentropic exponents of real gases and application for the air at temperatures from 150 K to 450 K. *Acta Mechanica*, 65(1-4):81–99, January 1987. doi: 10.1007/bf01176874.

[4] J. Leachman, R. Jacobsen, Steve Penoncello, and E. Lemmon. Fundamental equations of state for parahydrogen, normal hydrogen, and orthohydrogen. *Journal of Physical and Chemical Reference Data - J PHYS CHEM REF DATA*, 38, 09 2009. doi: 10.1063/1.3160306.

[5] Chris D. Muzny, Marcia L. Huber, and Andrei F. Kazakov. Correlation for the viscosity of normal hydrogen obtained from symbolic regression. *Journal of Chemical & Engineering Data*, 58(4):969–979, March 2013. doi: 10.1021/je301273j.

[6] Ding-Yu Peng and Donald B. Robinson. A new two-constant equation of state. *Industrial Engineering Chemistry Fundamentals*, 15(1):59–64, February 1976. doi: 10.1021/i160057a011.

[7] P. Schley, E. von Lavante, D. Zeitz, M. Jaeschke, H. Dietrich, and B. Nath. Simulation of critical nozzle flow considering real gas effects. In *Flomeko 2000 - IMEKO TC9 Conference*, 2000.

[8] Roland Span, Eric W. Lemmon, Richard T Jacobsen, Wolfgang Wagner, and Akimichi Yokozeki. A reference equation of state for the thermodynamic properties of nitrogen for temperatures from 63.151 to 1000 K and pressures to 2200 MPa. *Journal of Physical and Chemical Reference Data*, 29(6):1361–1433, November 2000. doi: 10.1063/1.1349047.

[9] William Sutherland. The viscosity of gases and molecular force. *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science*, 36(223):507–531, December 1893. doi: 10.1080/14786449308620508.

[10] W. Wagner and R. Span. Special equations of state for methane, argon, and nitrogen for the temperature range from 270 to 350 k at pressures up to 30 MPa. *International Journal of Thermophysics*, 14(4):699–725, July 1993. doi: 10.1007/bf00502103.